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COMMERCIAL SOLVENTS CORPORATION

TERRE HAUTE, INDIANA

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November 14, 1952
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Report No. Q-4
(Quarterly Summary)

SUBJECT: ONR Nitropolymer Research

CONTRACT: Nonr-397(00)

PERIOD COVERED: August 1, 1952 to October 31, 1952

SUBMITTED BY: John T. Minor

APPROVED BY: Jerome Martin
Jerome Martin
Director of Research

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SECURITY INFORMATION

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COMMERCIAL SOLVENTS CORP. Report No. Q-4

TABLE OF CONTENTS

SECURITY INFORMATION

CONTRACT FULFILLMENT

This quarterly report is submitted in partial fulfillment of Contract Nonr-397(00).

SECURITY INFORMATION

COMMERCIAL SOLVENTS CORP. Report No. Q-4

I. SUMMARY

A. This quarterly summary report is the fourth under Contract Nonr-397(00) and covers the period from August 1, 1952 to October 31, 1952. The object of this contract is as follows: Shall conduct research in the synthesis of polynitro compounds to include, but not necessarily be limited to, a review of the chemistry and the processes of preparation of the more useful products of research from the nitropolymer program and investigate the application of processes not now employed in the preparation.

B. The more important results and conclusions of the work reported are presented below:

1. The high pressure nitrations of cyclohexanone with 30% nitric acid gives adipic acid only. The yields run up to 49%.

2. 2-Nitrobutane can be nitrated with 62% nitric acid at 180°C. and 1000 p.s.i.g. to give 2,2-dinitrobutane in 10% yield.

3. When nitric acid and 1-nitropropane are reacted under pressure at 180°C., there is considerable gas formed and no isolatable product. Small amounts of 1-nitropropane can be recovered.

4. 2,2-Dinitropropane and 2-nitropropane are the major products when propane and nitric acid are reacted under pressure.

5. A process is given for pilot plant production of 2,2-dinitropropanediol on a 0.15 lb-mol scale.

6. The material and labor cost for DNPD pilot plant production is $11.44 per lb.

II. HIGH PRESSURE NITRATION STUDIES

A. CYCLOHEXANONE

In attempts to introduce the nitro group into a cyclic compound, or to break the cyclic chain and retain nitro groups, cyclohexanone was used as the example of the cyclic ketones. When cyclohexanone and 30% nitric acid were reacted for 20 min. at 1000 p.s.i.g. in the high pressure system, the only product isolated was adipic acid, m.p. 150-151°C. Seven temperatures were used, ranging from 80°C. to 180°C. At the higher temperatures, the yields were lower and more gas was formed.

Temperature, °C.	Yield of Adipic Acid
80	39
90	40
100	45
120	43
140	49
160	37
180	29

SECURITY INFORMATION

A run was made using 90% nitric acid in one stage of the pump and cyclohexanone dissolved in acetic anhydride in the other stage of the pump. Directly following the mixing point, at room temperature, excessive heating took place and after 40 min. of the run the line plugged from decomposition residue. No product could be isolated.

B. 2-NITROBUTANE

2-Nitrobutane was nitrated in the pressure system at 1000 p.s.i.g. and 180°C. with 62% nitric acid. When the nitric acid to nitrobutane mole ratio was 3 to 1, a 10% yield of 2,2-dinitrobutane was obtained. Of the original 2-nitrobutane, 36% was recovered.

C. 1-NITROPROPANE

In an attempted pressure nitration of 1-nitropropane at 1000 p.s.i.g. and 180°C. with 62% nitric acid there was excessive gassing. Of the 4550 ml. of total material fed to the reactor, only 2770 ml. were recovered as product. From this reaction product, the only compound obtained was 10% of the original 1-nitropropane.

D. PROPANE

The investigation of the preparation of DNP (2,2-dinitropropane) from propane and nitric acid was undertaken so that a comparison could be made of the cost of producing DNP by the oxidative-nitration reaction* and directly from propane. When 60% nitric acid and propane were reacted at 180°C., 1000 p.s.i.g. pressure, in a 1 to 1 mole ratio, local heating or "hot spots" became uncontrollable. When 40% nitric acid was used under similar conditions, DNP and 2-nitropropane were the only products isolated. The quantity of 2-NP produced under these conditions is about 2.5 moles for each mole of DNP.

This work is not completed and more favorable conditions will be studied when the reaction system is revised for better heat control.

III. PILOT PLANT PROCESS FOR DMPD (2,2-DINITRO-1,3-PROPANEDIOL)

A. DISCUSSION

We have examined the DMPD preparation from nitromethane and formaldehyde using the oxidative-nitration reaction. It was thought desirable to find an extractant other than ethyl ether and a more readily available recrystallizing solvent than 1-chloro-1-nitroethane. The use of these two solvents does give a very high grade product, but the use of ether in the pilot plant is hazardous and undesirable. The use of isopropyl acetate as the extracting solvent and ethylene dichloride as the recyrstallizing solvent produces a product of acceptable quality. Isopropyl

*Commercial Solvents Report Q-3, p. 2.

acetate has a favorable distribution coefficient, as does ethyl acetate, but was preferred as it forms a minimum boiling azeotrope with water, thus eliminating chemical drying of the extract. One gram of DNPD can be recrystallized from 1.5 to 2.0 ml. of ethylene dichloride with good recovery.

B. EXPERIMENTAL

1. Silver Nitrate Recovery

The silver cake filtered from previous runs, equivalent to 0.3 mol, is placed in a stainless steel or ceramic vessel which can be heated and agitated. The 27 lbs. (0.43 mol) of nitric acid, calculated to weight from the carboy analysis, is added in portions in a well ventilated hood. When the reaction has subsided, the solution is heated to the boiling point with agitation, and this is continued until all the metal has dissolved. The solution is made up to 150 lbs. total weight with chlorine-free water and the pH is adjusted to 5.9 with sodium hydroxide. A 100-g. sample is taken, diluted to one liter and aliquots titrated with standard ammonium thiocyanate solution using a ferric sulfate indicator. The amount of silver nitrate present in the solution is calculated and if not 51.0 lbs. (0.30 mol), it is made up to that weight by adding silver nitrate crystals. This solution is then ready for the reaction when cooled to 15°C.

2. Salt Preparation

A vessel with efficient cooling is required for this step. When unavailable, part of the water added must be replaced by crushed ice. Add to the vessel 9.2 lbs. (0.15 mol) of nitromethane, 9.0 lbs. (0.30 mol) of formaldehyde as 24.3 lbs. of 37% solution, and 47 lbs. of water. Agitate and chill the solution and slowly add 6.6 lbs. (0.16 mol) of tech. sodium hydroxide dissolved in 13 lbs. of water, keeping the temperature below 30°C. Cool before using to 15°C.

3. Oxidative-Nitration Reaction

The silver nitrate solution is placed in a vessel equipped with cooling coils or jacket and an efficient stirrer. The salt solution is added as rapidly as possible, holding the temperature below 25°C., and the resulting slurry is stirred for 1/2 hr. The precipitated silver should be spongy in nature and green in color for easy filtering.

4. Product Isolation

The reaction mixture is filtered and the silver cake washed and returned for silver nitrate recovery. The filtrate is extracted by means of a packed column or batchwise by three extractions of isopropyl acetate, each volume of solvent being equal to one-half the volume of the extracted solution. The raffinate is discarded if no silver ions are present. If silver is present, it may be recovered by making the raffinate basic with hydroxide and filtering. The filtrate is now discarded and the precipitate of silver oxide is added to the silver cake for recovery.

No drying of the isopropyl acetate extract is necessary as the water-isopropyl acetate azeotrope will remove the dissolved water when concentrating. The extract is concentrated to the minimum volume, trying to remove all the acetate and keeping the liquid temperature below 45°C. The residue is then dissolved in

25 lbs. of ethylene dichloride at 80-82°C., filtered and treated with char if necessary and cooled to 5°C. After filtering off the crystallized DNPD, there should be 12 to 15 lbs. of dried DNPD. A second crop is obtained by evaporating and cooling the combined mother liquors.

C. MATERIAL AND LABOR COSTS

The cost of starting materials and losses are tabulated for a 0.15 lb-mol reaction. Labor is estimated to require two operators for 24 hrs. plus one-third the time of a supervisor, or $5.10 per hour. The yield is based on 50%, or 12.5 lbs. of DNPD.

Nitromethane	$2.30
Formaldehyde	.63
Sodium hydroxide	.25
Sodium nitrite	.83
Silver nitrate (2% loss)	8.68
Nitric acid	1.49
Isopropyl acetate (10% loss)	5.30
Ethylene dichloride (40% loss)	1.20
Total	20.68
Labor	122.50
Total cost for labor and material	$143.18
Labor and material cost per lb. DNPD	$11.44

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